ELECTRICAL CONDUCTIVITY OF HYDROGENATED AND NITROGEN-DOPED NANODIAMOND FILMS

An-Jen Cheng, Maurice Clark, Yen-Kang Liu, Yu-Chun Chen, and Yonhua Tzeng
Department of Electrical and Computer Engineering, Auburn University, Auburn, Alabama 36849 USA

Keywords: Conductivity, nanodiamond, hydrogenation, nitrogen doping

Electrical conductivity of undoped and nitrogen doped nanodiamonds has been characterized. Nanodiamond films were deposited on molybdenum, silicon dioxide, and silicon by means of microwave plasma assisted chemical vapor deposition in gas mixtures of methane and argon with or without hydrogen and/or nitrogen additives. Electrical conductivity of nanodiamond films was measured by either (i) directly measuring the conductivity of a metal/nanodiamond/metal sandwich test structure or (ii) applying a electrical current through two terminals of a van der Pauw test structure while measuring the voltage across the other two terminals on corners of a nanodiamond film that was deposited on the electrically insulating surface of a substrate.

Nanodiamond films with thickness of about one micrometer were deposited in gas mixtures of (2% H_2, 1% CH_4, 97% Ar) or (1% CH_4, 99% Ar) by means of microwave plasma CVD. Effects of post deposition heat treatment in air at 350°C for 30 min on electrical conductivity of these undoped nanodiamond films were analyzed by measuring the electrical conductivity of as-deposited nanodiamond films and that of the same nanodiamond films after being heat treated in air. The heat treated nanodiamond films were later exposed to a hydrogen plasma and subsequently measured for their electrical conductivities in comparison with that for the as-deposited nanodiamond films and the heat treated nanodiamond films. The as-deposited nanodiamond films with 2% hydrogen additives in the gas mixture was found to have much higher conductivities than the films without hydrogen additive by more than one order of magnitude.

After both films were heat treated in air, electrical conductivities were found to be similar in values. It is believed that the heat treatment removed hydrogen in both nanodiamond films deposited in the gas mixture with 2% hydrogen additive and the nanodiamond films deposited without hydrogen additive in the gas mixture during the growth. Nanodiamond deposited with or without 2% hydrogen additive both showed the same effects of post-heat treatment hydrogenation on increasing electrical conductivity. The electrical conductivity did not increase to the same level after the nanodiamond films were exposed to a hydrogen plasma as that for the as-deposited nanodiamond films. The increase in conductivity for heated nanodiamond after being exposed to a hydrogen plasma was much less than that for a large-grained polycrystalline diamond film because of the much smaller grain sizes and much higher density of grain boundaries for nanodiamond films (ref. 1 and ref. 2).

Examples of I-V curves measured for an as-deposited nanodiamond film deposited in a gas mixture with 2% hydrogen additive are shown in Figure 1. Conductivity of the as-deposited nanodiamond film was found to be $1.11 \times 10^{-6}\ \Omega^{-1}cm^{-1}$ (Fig. 1, curve (a)). It decreased by more than two orders of magnitude to $6.67 \times 10^{-9}\ \Omega^{-1}cm^{-1}$ after being heated in air (Fig. 1, curve (b)) and then increased to $1.33 \times 10^{-8}\ \Omega^{-1}cm^{-1}$ after being exposed to a hydrogen plasma (Fig. 1, curve (c)).

I-V curves for a nanodiamond film deposited in a gas mixture without hydrogen additive are shown in Figure 2. Conductivity for the as-deposited nanodiamond film was found to be $2.49 \times 10^{-8}\ \Omega^{-1}cm^{-1}$ (Fig. 2, curve (a)). It decreased to $6.02 \times 10^{-9}\ \Omega^{-1}cm^{-1}$ after being heated in air (Fig. 2, curve (b)) and then increased again to $1.75 \times 10^{-8}\ \Omega^{-1}cm^{-1}$ after being exposed to a hydrogen plasma (Fig. 2, curve (c)).

Nitrogen doped nanodiamond films were produced by microwave plasma CVD with up to 40% of nitrogen additive in the 1% methane-argon gas mixture. Nitrogen doping was found to increase the electrical conductivity of the nanodiamond in a way similar to what was previously reported by the research group of Argonne National Laboratory (ref. 3). However, the conductivity of 20% nitrogen doped nanodiamond deposited by our group was found to be much lower than the value reported in reference 3.

The nitrogen doped nanodiamond film, that was deposited at a gas pressure of 100 Torr and at the substrate temperature of 700°C using 800W microwave power, was measured to have a conductivity of only $2.76 \times 10^{-1}\ \Omega^{-}$

^{1}cm^{-1}. Nanodiamond deposited at a lower microwave power of 600W resulted in a higher conductivity of 7.76×10^{-1} Ω^{-1}cm^{-1}, which was still much lower than the value reported in reference 3. Further optimization of our deposition process in an attempt to achieve the previously reported much higher electrical conductivity and the re-confirmation of the much higher conductivity reported in reference 3 are being conducted.

Details of specimen preparation processes, experimental measurement procedure, and the analysis of the effects of post-deposition heat treatment in air, hydrogenation and nitrogen doping on electrical conductivity of nanodiamond films will be reported and discussed in this presentation. High conductivity nanodiamond films are desirable for electrochemical applications.

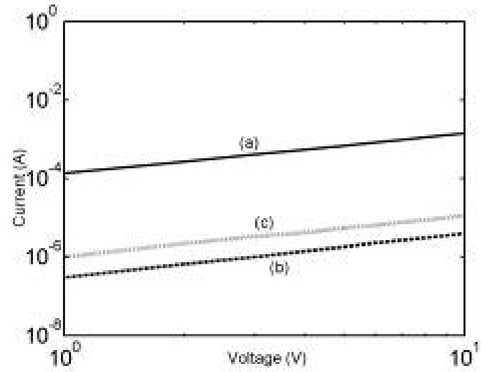

Figure 1. I-V curves for a nanodiamond film deposited in a gas mixture of 1% methane, 2% hydrogen, and 97% argon. (a) as-deposited with resistivity = 9.0×10^5 ohm-cm; (b) after heat treatment in air with resistivity = 1.5×10^8 ohm-cm; (c) after being exposed to a hydrogen plasma with resistivity = 7.5×10^7 ohm-cm.

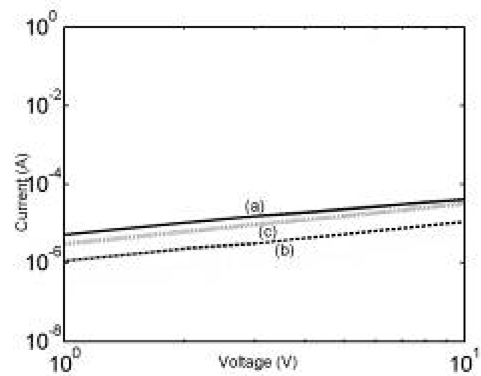

Figure 2. I-V curves for a nanodiamond film deposited in a gas mixture of 1% methane and 99% argon. (a) as-deposited with resistivity = 4.0×10^7 ohm-cm; (b) after heat treatment in air with resistivity = 1.7×10^8 ohm-cm; (c) after being exposed to a hydrogen plasma with resistivity = 5.7×10^7 ohm-cm.

References:

1. Landstrass, M. I.; and Ravi, K. V., “Resistivity of chemical vapor deposited diamond films,” *Applied Physics Letters*, Vol. 55, No. 10, 975-977 (1989).
2. Tzeng, Y., et al., “High electrical resistivity diamond films deposited from an oxyacetylene flame,” *Applied Physics Letters*, Vol. 57, No. 8, 789-791 (1990).
3. Bhattacharyya, S., et al., “Synthesis and characterization of highly-conducting nitrogen-doped ultrananocrystalline diamond films,” *Applied Physics Letters*, Vol. 79, No. 10, 1441-1443 (2001).